

# Laser detection of the rare isotope $^3\text{He}$ at concentrations as low as $10^{-9}$

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Received July 16, 1990; accepted November 2, 1990

The method of collinear laser photoionization of atoms in a modulated fast beam is used to detect the rare isotope  $^3\text{He}$ , with high-repetition-rate lasers being applied to improve the detection sensitivity. The method has made it possible to detect  $^3\text{He}$  at relative abundances as low as  $10^{-9}$ .

There has been considerable interest recently in the development of laser techniques for detecting rare long-lived isotopes.<sup>1,2</sup> Such a detection presupposes, first, an extremely high isotopic selectivity of the process of interaction between laser radiation and the rare isotope to be detected, for a single atom of the rare isotope has to be detected against the background of  $10^{10}$ – $10^{16}$  atoms of other isotopes of the same element, and second, a detection sensitivity high enough to provide for a reasonable analysis time and sample size.

Methods suggested and experimentally investigated for the detection of rare isotopes include the laser resonance atomic photoionization technique,<sup>3–5</sup> the photon burst technique,<sup>6–8</sup> the selective atomic deceleration technique,<sup>9</sup> the selective atomic deviation technique,<sup>10,11</sup> the ground-state depletion technique,<sup>12,13</sup> and the method of collinear laser photoionization of atoms in an accelerated beam.<sup>14–16</sup> However, the selectivity of the detection of rare-isotope atoms achieved up to now with purely laser techniques has been no better than  $10^6$ . The detection selectivity can be greatly improved by combining laser technique with traditional mass spectrometry. However, as the selectivity grows higher, the problem of the sensitivity of such a detection becomes more important.

In this Letter collinear laser atomic photoionization is used in conjunction with the time-of-flight separation of isotopic atoms in a pulsed beam to detect the rare isotope  $^3\text{He}$ .

The idea of collinear laser atomic photoionization technique<sup>14</sup> is that selective laser excitation of atoms to a Rydberg state, followed by their electric-field ionization, occurs in a fast beam obtained through the charge exchange of a beam of ions accelerated preliminarily in a specified potential  $U_A$ . The collinear excitation of atoms in such a beam gives rise to an additional kinematic isotope shift in the absorption spectrum of any element in any transition, which is many times the natural isotope shift. Owing to velocity bunching, the Doppler absorption linewidth can be reduced to the radiative width.<sup>17,18</sup> This allows the atoms of a rare isotope to be excited in an extremely selective fashion.

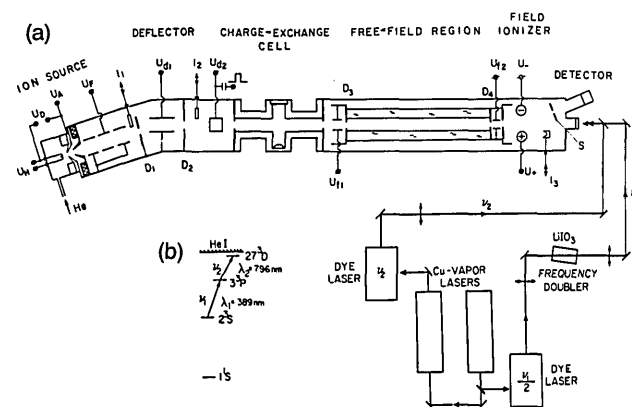
Experiments on detecting the rare isotope  $^3\text{He}$  (Refs. 16 and 19) have, however, shown that the capabilities of the technique are limited by the background

noise signal due to collisions between the accelerated atoms of the abundant isotope  $^4\text{He}$  and residual gas molecules. At a residual gas pressure in the vacuum system of  $10^{-7}$  Torr, the level of the background noise signal corresponded to a  $^3\text{He}$  abundance of  $10^{-6}$ .

In Ref. 20 the authors made use of an additional time-of-flight isotope separation to combat the background noise. This made it possible to suppress the noise signal to a large degree and detect reliably the rare isotope  $^3\text{He}$  in samples with a relative abundance as low as  $10^{-7}$ , with this value being limited by the counting rate of the rare-isotope atoms and not by the background noise.

In this Letter we have raised the counting rate, and hence improved the sensitivity of the technique, by a factor of  $10^2$ , mainly as a result of using high-repetition-rate lasers.

The experimental setup is shown schematically in Fig. 1(a). A beam of He ions accelerated to an energy of  $eU_A = 3.9$  keV is produced by a hot-cathode ion source and then focused with a single electrostatic lens and deflected by means of a deflector  $d_1$  to free it from the neutral component. The deflected beam is then made to pass through a plane capacitor  $d_2$  that is used as an ion-beam modulator. By applying a voltage of  $U_{d2} = 50$  V across capacitor  $d_2$ , the ions can be com-



pletely deflected from the axis of the setup. The modulation occurs by means of short square pulses returning the ion beams to the axis. The time of flight from the modulator to the detector is  $4.5 \mu\text{s}$  for  $^3\text{He}$  and  $5.2 \mu\text{s}$  for  $^4\text{He}$ . With the modulating pulse duration  $\tau_p$  being as short as  $0.5 \mu\text{s}$ , the isotopes are separated completely.

Downstream from the modulator the ion beam enters a charge-exchange cell containing K vapor at a temperature of  $160^\circ\text{C}$  in which approximately 40% of the ions exchange their charge to become neutral atoms, with some 75% of the atoms being produced in the  $2^3S$  triplet state.<sup>21</sup> The ions that failed to exchange their charge and the atoms produced in highly excited states are extracted from the beam by the electric field (9 kV/cm in strength) of a filtering capacitor  $f_1$ . Neutral atoms enter a 1-m-long field-free region, where they undergo two-step laser excitation from the  $2^3S$  metastable state to the  $27^3D$  Rydberg state through the  $3^3P$  intermediate level. Excitation occurs when a group of  $^3\text{He}$  atoms ( $\tau_p = 0.5 \mu\text{s}$ ; the group is 25 cm long) is at the exit of the field-free region (diaphragm  $D_4$ , 2 mm in diameter).

The Rydberg atoms entering the electric field of the two cylinders + and - (usually  $U_{f2} = 0$ ) are ionized and deflected by the same field onto an adjustable slit S with a secondary electron multiplier behind it.

The  $^3\text{He}^+$  ions are detected during a time interval of  $\tau_{\text{det}} = 0.6 \mu\text{s}$  by means of a gated counting system  $4.5 \mu\text{s}$  (delay time  $t_d$ ) after the modulating pulse is applied to capacitor  $d_2$ . The background ions that result from collisions involving  $^4\text{He}$  atoms arrive at the detector  $5.2 \mu\text{s}$  after the modulating pulse.

The Rydberg states are excited with two pulsed dye lasers that generate at frequencies  $\nu_2$  and  $(1/2)\nu_1$ . Radiation at  $\nu_1$  is then obtained by frequency doubling in a  $\text{LiIO}_3$  crystal.

The dye lasers are pumped by two copper-vapor-laser tubes, one used as an oscillator and the other as an amplifier. The repetition frequency of the laser pulses is 8.6 kHz, and their duration is 18 ns. The dyes used absorb only the yellow copper-vapor-laser line (578 nm). The pump-pulse energy of each dye laser is  $Q_{1,2} = 0.5 \text{ mJ}$ . In this case the energies of the laser pulses at frequencies  $\nu_1$  and  $\nu_2$  are  $Q\nu_1 = 0.6 \mu\text{J}$  and  $Q\nu_2 = 25 \mu\text{J}$  at the entrance to the vacuum system, the delay time between them being 5 ns. The radiation bandwidths at the frequencies  $\nu_1$  ( $\Delta\nu_1 = 0.8 \text{ cm}^{-1}$ ) and  $\nu_2$  ( $\Delta\nu_2 = 0.5 \text{ cm}^{-1}$ ) are much smaller than the isotope shift values in the absorption spectrum of the beam ( $\delta\nu_{1,\text{is}} = 7.1 \text{ cm}^{-1}$ ,  $\delta\nu_{2,\text{is}} = 3.2 \text{ cm}^{-1}$ ), which allows for an exceptionally high selectivity of laser excitation.

To illustrate, the spectral selectivity of excitation of the rare isotope  $^3\text{He}$  is limited by absorption on the wing of the abundant isotope  $^4\text{He}$ . If  $\Gamma$  is the homogeneous half-width describing the Lorentzian wing of the absorption line, and the condition  $\Gamma < \Delta\nu_{1,2} \ll \delta\nu_{1,2,\text{is}}$  is satisfied, the selectivity of excitation in each step is defined by the expression  $S_{1,2} = (\delta\nu_{1,2,\text{is}}/\Gamma)^2(2\Gamma/\Delta\nu_{1,2})$ .<sup>1</sup> For the atomic He transitions used, the radiative half-width  $\Gamma$  is determined by the lifetime of the intermediate level  $3^3P$  and is equal to 0.84 MHz. In this case laser excitation selectivities in the first and second step are  $4.5 \times 10^6$  and  $1.4 \times 10^6$ , respectively. The

total two-step excitation selectivity must then be no worse than  $S = S_1 \times S_2 = 6.3 \times 10^{12}$ .

Figure 2 illustrates the isotopic selectivity of the process of laser photoionization of accelerated He atoms in a modulated beam. Figure 2(a) shows the photoion signal as a function of the second-step laser frequency  $\nu_2$ , with the first-step laser frequency  $\nu_1$  being tuned to resonance with the  $^4\text{He}$  isotope. The ions reach the detector  $5.2 \mu\text{s}$  after the modulating pulse is applied to deflector  $d_2$ . Figure 2(a) shows the ion signals due to the excitation of the  $27^3D$  and  $28^3D$  states in He. The signals due to the excitation of the  $n^3S$  states are observed at lower voltages  $U_+$  and  $U_-$ .<sup>16</sup> Figures 2(b) and 2(c) present the photoion signals from  $^3\text{He}$  at relative abundances of  $10^{-6}$  and  $1.2 \times 10^{-7}$ , respectively. The signals are obtained with the frequency  $\nu_1$  shifted  $7.1 \text{ cm}^{-1}$  to the red side and with a delay time  $t_d$  of the counting system of  $4.5 \mu\text{s}$ .

Figure 3 presents the counting rate of  $^3\text{He}$  ions as a function of the isotope concentration in the gas. The function is a straight line, and the results of our measurements of  $^3\text{He}$  isotope concentrations in air and commercial-grade He gas are in complete agreement with published data.<sup>22</sup>

The counting rate of photoions of a rare isotope at a concentration of  $C$  is  $N = I_3\tau_p f \eta C$ , where  $I_3$  is the continuous atomic beam current,  $\tau_p$  is the beam current pulse duration,  $f$  is the laser pulse repetition frequency, and  $\eta$  is the efficiency of exciting the atoms and detecting the photoions produced. For  $f = 8.6 \text{ kHz}$ ,  $I_3 = 2.3 \times 10^{11} \text{ s}^{-1}$ ,  $\tau_p = 0.5 \mu\text{s}$ ,  $C = 10^{-6}$ , and  $\eta = 0.01$ , the  $^3\text{He}$  photoion counting rate is  $N = 10$  counts per second. The background noise signal that is manifested in Figs. 2(b) and 2(c) has no relation to laser radiation and corresponds to a  $^3\text{He}$  concentration of  $10^{-9}$ . The laser excitation efficiency  $\eta$  in the present research was lower by a factor of 10 than that reported in Ref. 20, where the dye lasers were pumped by a

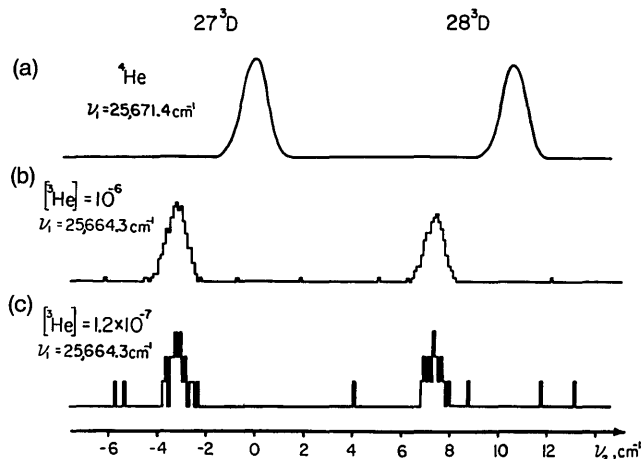


Fig. 2. Ion signal as a function of the second-step laser frequency  $\nu_2$ . The variation rate of the frequency  $\nu_2$  is  $3 \text{ cm}^{-1}/\text{min}$ . (a) First-step laser frequency in resonance with the  $^4\text{He}$  isotope;  $t_d = 5.2 \mu\text{s}$ . (b) First-step laser frequency in resonance with the  $^3\text{He}$  isotope. The counting system is gated to detect the  $^3\text{He}$  ions ( $t_d = 4.5 \mu\text{s}$ ). The averaging time is 2 sec, and the isotope concentration  $[^3\text{He}]$  is  $10^{-6}$ . (c) The same as (b) but for an isotope concentration  $[^3\text{He}]$  of  $1.2 \times 10^{-7}$ .

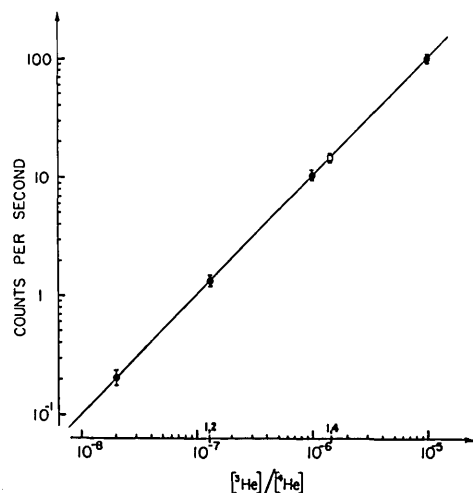


Fig. 3. Photoion signal from the  $^3\text{He}$  isotope ( $t_d = 4.5 \mu\text{s}$ ) as a function of the isotopic concentration  $[^3\text{He}]$ . Filled symbols, calibration mixtures and the Soviet commercial-grade He gas used to prepare the mixtures; open symbol, He obtained from atmospheric air.

XeCl laser ( $Q_{1,2} \approx 10 \text{ mJ}$ ). This is explained by the fact that we failed here to saturate the optical transitions in He because we used copper-vapor-laser pumps ( $Q_{1,2} = 0.5 \text{ mJ}$ ) and frequency doubling for the first excitation step. In our experimental conditions the efficiency of detecting the rare isotope atoms, determined as the ratio of the counted number of atoms  $N$  to the total number of atoms in the beam, equal to  $CI_3$ , was  $4.3 \times 10^{-5}$ . The optical transitions could be saturated either by increasing the pumping laser power or by narrowing the radiation spectra of the dye lasers. This would raise the rare-isotope photoion counting rate 10 times and make the background noise level correspond to a  $^3\text{He}$  concentration of  $10^{-10}$ .

To measure the selectivity of the time-of-flight isotope separation in the absence of laser photoionization, we could cool the charge-exchange cell, switch off the filtering voltage  $U_{f1}$ , and set the voltages  $U_+$  and  $U_-$  so as to direct the modulated ion beam through the slit onto the detector. The modulation of the ion beam made it possible to separate the  $^3\text{He}$  and  $^4\text{He}$  ions, but naturally it could not help separate the  $^3\text{He}^+$  ions from the  $\text{HD}^+$  and  $\text{H}_3^+$  ones. It is usually these molecular ions that limit the possibility of detecting  $^3\text{He}$  by traditional mass-spectrometric techniques.<sup>22</sup> In our case the ion signal for a mass  $M = 3$  ( $t_d = 4.5 \mu\text{s}$ ) was  $10^{-4}$  of that for  $M = 4$  ( $t_d = 5.2 \mu\text{s}$ ). This agrees well with the background noise signal's decreasing by a factor of  $10^4$  (from  $10^{-6}$  to  $10^{-10}$ ) as a result of adding time-of-flight isotope separation to the process of laser photoionization and means that the remaining background noise signal is due to the fast  $\text{H}_3$  and  $\text{HD}$  molecules colliding with the residual gas molecules and can apparently be greatly reduced by suppressing the production of hydrogen in the ion source. Further suppression of the background noise can only be achieved by reducing the residual gas pressure in the system.

The counting rate of photoions of a rare isotope at a concentration of  $C = 10^{-10}$  in the case of saturated

optical transitions ( $\eta = 0.1$ ) should be equal to 36 counts per hour. The sensitivity can be improved only by increasing the current  $I_3$ . Note, however, that while modulating the accelerated beam, we use laser excitation only in part of the field-free region. By using, with the same current  $I_3$ , magnetic mass separation, for example, instead of time-of-flight separation, one can increase the counting rate four times.

The gas flow in the course of the analysis was  $1 \text{ cm}^3/\text{h}$  under normal conditions and could be reduced considerably through the use of a more efficient ion source.

In conclusion, the method suggested here allows one to measure the  $^3\text{He}/^4\text{He}$  isotope ratio, which ranges in various natural terrestrial objects between  $10^{-4}$  and  $10^{-10}$ .<sup>22</sup> The method may also prove useful in detecting other rare isotopes.

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